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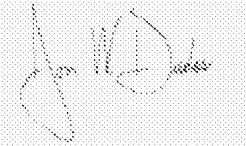
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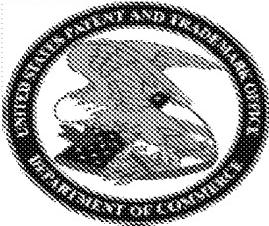
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07/29/03

PTO/SB/16 (10-01)

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This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 CFR 1.53(c).

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 Additional inventors are being named on the 1 separately numbered sheets attached hereto**TITLE OF THE INVENTION (500 characters max)****SELECTIVE FUNCTIONALIZATION OF CARBON NANOTUBES**

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 Application Data Sheet. See 37 CFR 1.76**METHOD OF PAYMENT OF FILING FEES FOR THIS PROVISIONAL APPLICATION FOR PATENT** Applicant claims small entity status. See 37 CFR 1.27.

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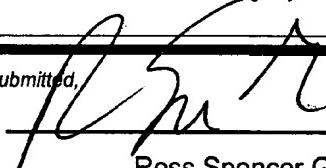
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The invention was made by an agency of the United States Government or under a contract with an agency of the United States Government.

Robert A. Welch Foundation C-0689, NASA-JSC-NCC-9-77,
NASA TiiMS NCC-01-0203 CFDA #43.001, NSF (DMR-0073046
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Respectfully submitted,

Date 07/29/2003

SIGNATURE 

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REGISTRATION NO.
(if appropriate)
Docket Number:

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SELECTIVE FUNCTIONALIZATION OF CARBON NANOTUBES

The present invention was made in connection with research pursuant to grant numbers: Robert A. Welch Foundation C-0689, NASA-JSC-NCC-9-77, NASA TiiMS NCC-01-0203 CFDA #43.001, NSF (DMR-0073046 and EEC-0118007) and AFOSR (F49620-01-1-0364).

FIELD OF INVENTION

The present invention relates generally to carbon nanotubes. More specifically, the invention relates to methods of functionalizing carbon nanotubes, separating carbon nanotubes by type, and populations of functionalized carbon nanotubes separated by type to yield novel compositions.

BACKGROUND OF THE INVENTION

Since their discovery in 1991, carbon nanotubes (CNTs) have been finding numerous applications in composite materials, sensors, molecular electronics, and other fields. For a general review of CNTs, see Ebbesen, *Annu. Rev. Mater. Sci.*, 1994, 24:235-264. Techniques of chemically functionalizing CNTs have greatly facilitated the ability to manipulate these materials, particularly for single-wall carbon nanotubes (SWNTs) which tend to assemble into rope-like aggregates. See Thess *et al.*, *Science*, 1996, 273:483-487.

Chemical functionalization of SWNTs is generally divided into two types: tube end functionalization (Chen *et al.*, *Science*, 1998, 282:95-98), and sidewall functionalization (PCT publication WO 02/060812 by Tour *et al.*).

Only recently, however, have methods to separate and identify SWNTs by type (where type is defined by their n,m roll-up vector). See O'Connell *et al.*, *Science*, 2002, 297:593-596; Bachilo *et al.*, *Science*, 2002, 298:2361-2366.

SUMMARY OF THE INVENTION

The present invention is directed toward a method of selectively functionalizing carbon nanotubes of a specific type or range of types, based on their electronic properties. The present invention is also directed toward methods of separating carbon nanotubes into populations of specific types or range(s) of types via selective functionalization and electrophoresis, and the novel compositions generated by such separations. Optionally, these isolated compositions can be thermally defunctionalized.

BRIEF DESCRIPTION OF THE DRAWINGS

For a more complete understanding of the present invention, and the advantages thereof, reference is now made to the following descriptions taken in conjunction with the accompanying figures, in which:

FIGURE 1 depicts a UV-vis-NIR Spectrum of sodium dodecylsulfate-suspended carbon nanotubes after the addition of various amounts of 4-chlorobenzenediazonium tetrafluoroborate (in mol/mol carbon) (A), wherein, under controlled conditions, semiconductor transitions are unaffected while metals react with high selectivity, and in an expanded view of the metallic region (b), the tetrafluoroborate salt causes some bathochromic shifting of the longer wavelength features due to changes in the surfactant adsorbed phase; and

FIGURE 2 depicts the Raman spectrum at 532 nm excitation showing the growth of the "disorder" mode with increasing functionalization from 0 (black), 5.6 (blue), to 22.4 (red) groups attached per 1000 carbon atoms (A), and wherein the intensity of the tangential mode (blue) x 0.1 decreases as resonance enhancement of the scattering event is lost with increasing reaction (B) and the disorder mode (yellow) increases sharply then decays due to the same loss of enhancement.

DETAILED DESCRIPTION

The present invention is directed toward a method by which carbon nanotubes can be chemically functionalized according to their precise electronic structure. While not intending to be bound by theory, it is believed that the process involves an exploitation of charge transfer stability at the nanotube sidewall to direct selective reaction of certain electronic structures over others. This method forms the basis for manipulating and separating carbon nanotubes by their electronic structure by chemical means which, in some embodiments, yields populations of carbon nanotubes having specific diameters, chiralities, and electronic properties. In other embodiments, populations of carbon nanotubes having specifically-tailored ranges of diameters, chiralities, and electronic properties are produced.

The problem of separating carbon nanotubes has been around since their initial synthesis in 1991. While there have been recent reports of separating SWNTs based on their electronic properties, there has been no successful demonstration of using electronic selectivity to accomplish this feat. In fact, electronic selectivity has, up to now, not been demonstrated.

Carbon nanotubes, according to the present invention, comprise single-wall carbon nanotubes (SWNTs), multi-wall carbon nanotubes (MWNTs), and combinations thereof. They can generally be of any length, diameter, chirality, or number of walls, as are currently available.

Selective Functionalization

In general, the process for selectively functionalizing the carbon nanotubes comprises:

- a) selecting a quantity of carbon nanotube material; b) suspending the carbon nanotube material in a solvent; and c) adding a chemical reactant that is able to selectively functionalize the carbon nanotube material based on the electronic properties of the nanotubes.

More specifically, the process for selectively functionalizing the carbon nanotubes comprises:

- a) selecting a quantity of carbon nanotube material;
- b) adding the carbon nanotube material to an aqueous surfactant solution and homogenizing to form a mixture comprising surfactant-suspended carbon nanotubes;
- c) adding a suitable diazonium species to the mixture in an amount which is suitable to react preferentially with the metallic and semi-metallic carbon nanotubes, but not with the semiconducting carbon nanotubes.

Surfactants, according to the present invention, can be any chemical agent which facilitates the dispersion of carbon nanotubes in water. Surfactants include, but are not limited

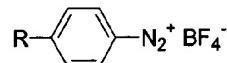
to, ionic surfactants, non-ionic surfactants, cationic surfactants, anionic surfactants, sodium dodecyl sulfate (SDS), sodium dodecylbenzene sulfonate (SDBS), sodium octylbenzene sulfonate, Triton X-100, dodecytrimethylammonium bromide (DTAB), and combinations thereof. However, organically-wrapped CNTs in an organic solvent could also be partners for this reaction with a diazonium salt in a selective coupling, provided the wrapped species are single nanotubes, or small bundles thereof, *i.e.*, on the order of 2-3 nanotubes, such that the individual nanotubes are accessible for the selective functionalization process.

In some embodiments of the present invention, the process of forming an aqueous mixture of surfactant-suspended carbon nanotubes comprises a homogenizing step. A homogenizing step, according to the present invention, can be any method which suitably homogenizes the mixture and renders at least some of the carbon nanotubes encapsulated in micellar-like assemblies.

In some embodiments of the present invention, the process of forming an aqueous mixture of surfactant-suspended carbon nanotubes further comprises ultrasonic assistance. Ultrasonic assistance can be provided by either an ultrasonic bath or an ultrasonic horn sonicator, typically operating at a power from between about 200 W to about 600 W. The duration of such ultrasonic assistance typically ranges from about 1 min to about 20 min.

In some embodiments of the present invention, the mixture of surfactant-suspended carbon nanotubes is centrifuged to separate the surfactant-suspended nanotube material from other material. In such embodiments, the other material gravitates to the bottom and the surfactant-suspended carbon nanotubes are decanted. In some embodiments of the present invention, the centrifugation is provided by an ultracentrifuge, and centrifugation is performed with an intensity which ranges generally from about 10,000 rpm to about 90,000 rpm, and for a duration which ranges generally from about 1 hour to about 6 hour.

In some embodiments of the present invention, aryl diazonium salts are used as the diazonium species. Suitable aryl diazonium salts include, but are not limited to,



where R is selected from the group consisting of halogen, nitro, cyano, alkyl, aryl, arylalkyl, hydroxy, carboxylic ester, carboxylic acid, thiocarbonate, amide, alkoxy, polyether, polyalkyl, hydroxy alkyl, and combinations thereof. Variations for "R" include: a) aliphatic chains or groups for nonpolar solvent solubility; b) polystyrene, polyethylene, polypropylene, etc. for incorporation

into composites or blends; c) electrically-conducting polymeric substituents (*i.e.*, polypyrrole or poly(phenylene vinylene)); d) polyether chain to increase water or alcohol solubility; e) carboxylic acid or carboxylate anion to increase water solubility; f) substituents that can cross-link polymers to form composites; g) R can be substituted at various positions on the aromatic ring (ortho, meta, para); h) there are multiple “R” groups; and, when present, use of Cl, Br, and I as leaving groups to attach to a metal surface or nanoparticle.

In some embodiments of the present invention, the aryl diazonium salt is first solubilized in water or another solvent, prior to adding it to the mixture of surfactant-suspended carbon nanotubes and allowing it to react with the nanotubes. In such embodiments, a stoichiometric amount of the aryl diazonium salt is added such that it reacts preferentially with the metallic (no bandgap) and semi-metallic (“Mod 3” nanotubes (where n-m = multiple of 3) possessing a very small bandgap, sometimes referred to as a “pseudo-gap,” that is curvature induced) carbon nanotubes, but not with the semiconducting carbon nanotubes.

In some embodiments of the present invention, Raman, absorption, and/or fluorescence spectroscopies are used to analyze the process during and after the reaction to indicate the reaction is selective favoring reaction of metallic and semi-metallic nanotubes first.

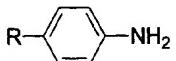
In some embodiments of the present invention, upon completion of the partial reaction (*i.e.*, reaction of the metallic and semimetallic nanotubes, but not the semiconducting nanotubes), a destabilizing agent can be added to destabilize the micellar assemblies and permit filtration. In some embodiments, the destabilizing agent used is N,N-dimethylformamide (DMF).

Since the selective reactivity is a function of the size of the band gap, continued addition of diazonium species will continue to react preferentially with the smallest band gap unreacted nanotubes present in the mixture. As these are preferentially reacted, the reaction will shift to the nanotubes with the next larger bandgap. Ultimately, if enough aryl diazonium salt is added, all of the nanotubes will react.

In some embodiments, however, the reaction selectivity is observed only present at low conversion, meaning that the surface coverage of the functional group is relatively small under selective conditions.

In some embodiments of the present invention, the diazonium species is generated *in situ* by reacting a substituted aniline species with an alkyl nitrite (or alternatively an inorganic

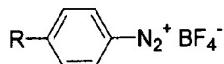
nitrite in the presence of an acid). Substituted aniline species, according to the present invention, have the general formula



where R (the substituent, or substituents in the case of multiple substitutions) is selected from the group consisting of halogen, nitro, cyano, alkyl, aryl, arylalkyl, hydroxy, carboxylic ester, carboxylic acid, thiocarbonate, amide, alkoxy, polyether, polyalkyl, hydroxyl alkyl, and combinations thereof.

Separation of carbon nanotubes

In some embodiments of the present invention, the aryl diazonium salts are selected such that they possess functional groups that are sensitive to changes in pH of the mixture of surfactant-suspended carbon nanotubes with have been partially reacted with said diazonium salt. In some embodiments of the present invention the diazonium salt is



where R is a hydroxyl group. At high pH values (e.g., > 10), the hydroxyl groups are deprotonated. In embodiments where the metals and semimetals have been preferentially functionalized, these species can be separated from the semiconducting carbon nanotubes using electrophoretic techniques like gel or capillary electrophoresis.

Thus, the reaction chemistry can be carried out such that all metallic nanotubes are selectively functionalized via phenol moieties, then separated by electrophoretic means yielding carbon nanotubes of specific type and which are not agglomerated in rope-like bundles. After recovery of the fractionated material, thermal treatment of the metallic nanotubes recovers their properties by driving off the functional groups.

The most immediate and obvious use of this invention is as a route to the separation of carbon nanotubes based on their electronic structure. By selectively functionalizing metallic nanotubes, or small band gap semiconducting nanotubes, the remaining species can, in some embodiments of the present invention, be separated by using changes in solubility that come about as a result of the functionalization. The increase in molecular weight can also be utilized

for this purpose. Other applications include fabrication of electronic devices consisting of all metallic nanotubes from a starting mixture of all electronic types. The diazonium reaction can be employed to generate highly functionalized materials.

No other method of functionalization of single walled carbon nanotubes has been shown to be selective to the electronic structure of the nanotube. This discovery is enabled by spectroscopic techniques for carbon nanotubes that have only recently become available. In particular, photoabsorption spectroscopy and fluorescence detection are employed to follow the reaction progression and monitor the effect of substituents addition to the nanotube electronic structure. Also, no other method exists to uniformly functionalize carbon nanotubes in solution. Previously, functionalized nanotubes consisted of highly functionalized nanotubes and unfunctionalized nanotubes. This observation was attributed to the bundling that occurs with nanotubes in the solid state.

The following examples are presented to further illustrate the invention and are not to be construed as unduly limiting the scope of this invention.

EXAMPLES

Example 1

Micelle-coated single walled carbon nanotubes are generated via homogenation of raw material and 1% of sodium dodecyl sulfate in water or D₂O for 1 hour, followed by sonication for 10 minutes. The solution is then centrifuged for 4 hours and decanted to generate the micelle-coated nanotubes. The pH is then adjusted to approximately 10, and various diazonium salts are added to the aqueous solution. The diazonium salt can be added as a solid directly to the decanted material, or the diazonium salt can be dissolved in water or D₂O, and added as a dilute solution. When a large excess of the salt is added, selectivity is not observed, but all the nanotubes are functionalized to a high degree. For selective functionalization, a dilute solution of the salt is prepared by solubilizing the diazonium salt in water or D₂O (roughly 1.5 M), and an aliquot of this solution is added to the nanotube decants with stirring. The reaction can be monitored by several spectroscopic techniques in order to determine the extent of functionalization. Once the functionalization is complete, the reaction mixture is diluted with

some organic solvent (acetone, DMF), and the flocculated nanotubes are then collected by filtration over a PTFE membrane. The collected solid is then washed with acetone and water to remove unreacted diazonium salt, diazonium decomposition side-products, and sodium dodecyl sulfate. The nanotube sample is then collected from the membrane and dried in a vacuum oven at 60°C.

The description here is not meant to be limiting. There are variations in concentration and reaction times, as well as methods for generating the intermediates that could be made. For example, one could generate the diazonium salts *in situ* from an aniline and an alky nitrite or an aniline and sodium nitrite/acid. Furthermore, the diazonium salts that respond best, to date, are aryl diazonium salts, however, this should not be construed as a limitation. Functional groups or substituents on the aryl ring can be varied to modify the hydrophilic and hydrophobic character of the nanotube addends to enhance separation efficacy or other properties.

The evidence for selective functionalization is observed in the UV-vis-NIR spectrum of the solution during and after the reaction. The reaction at the nanotube surface necessarily disrupts the photo-excitation process that normally gives the nanotube a prominent and sharp absorption maximum in this spectrum. FIGURE 1 shows that nanotubes having such a maximum at longer wavelengths (lower energy band gaps) are affected disproportionately at lower concentrations as their peaks decay. Smaller diameter nanotubes remain unaffected until larger reagent concentrations. FIGURE 2 shows the Raman spectrum at 532 nm excitation of the same solution after 0.05 mM reagent added. FIGURE 2A shows the low Raman shift region that normally possesses peaks representative of distinct nanotube diameters that are resonant with the laser. Only one is visible (the lowest wavelength transition of the group as indicated.) FIGURE 2B shows that the 'D-band' has increased – a characteristic of functionalization but the largest band-gap nanotubes (also shown) still fluoresce indicating the absence of functionalization (unperturbed electronic transitions.) All of this takes place at constant bulk pH = 10.

Example 2

See attached manuscript entitled "Selectivity of Electronic Structure in the Functionalization of Single Walled Carbon Nanotubes."

Although the invention has been described with reference to specific embodiments, these descriptions are not meant to be construed in a limiting sense. Various modifications of the disclosed embodiments, as well as alternative embodiments of the invention will become apparent to persons skilled in the art upon reference to the description of the invention. It should be appreciated by those skilled in the art that the conception and the specific embodiment disclosed may be readily utilized as a basis for modifying or designing other structures for carrying out the same purposes of the present invention. It should also be realized by those skilled in the art that such equivalent constructions do not depart from the spirit and scope of the invention as set forth in the appended claims.

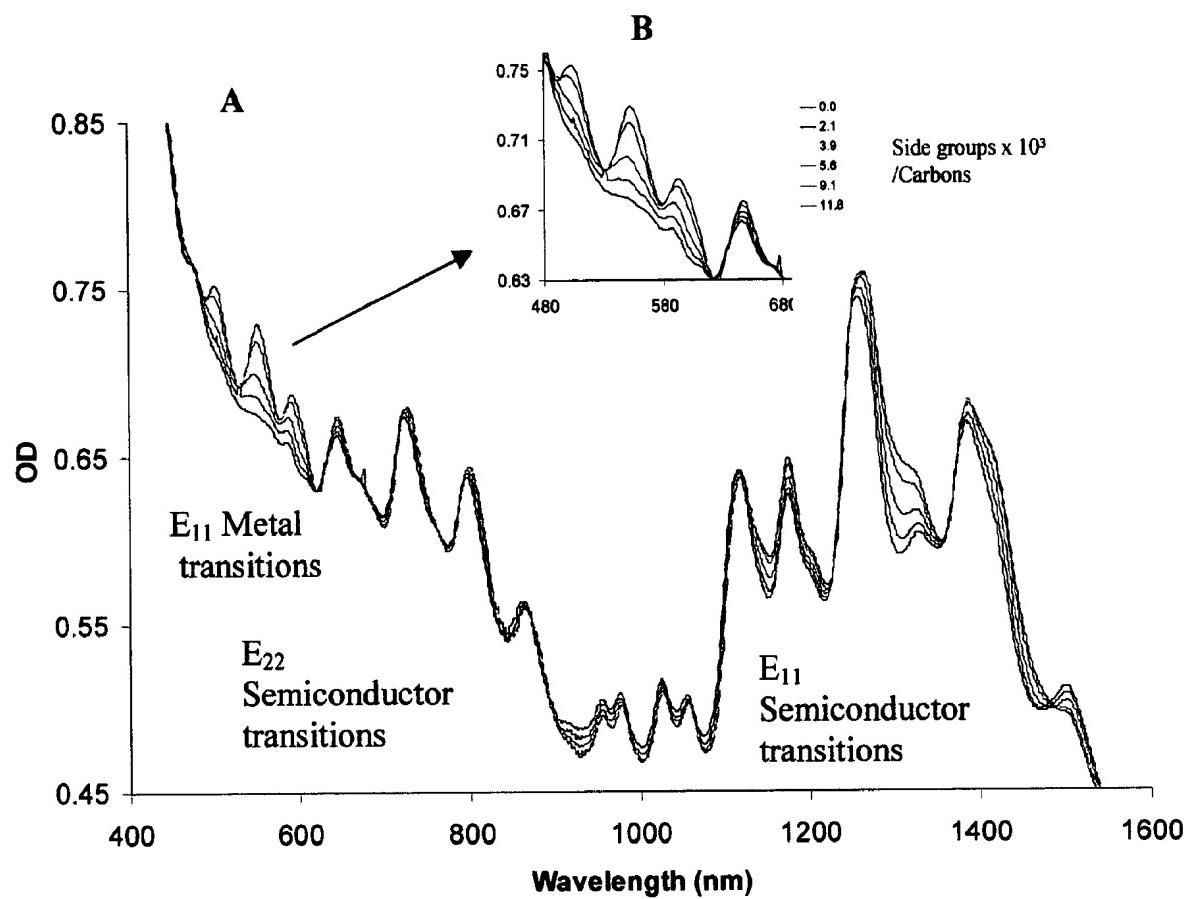
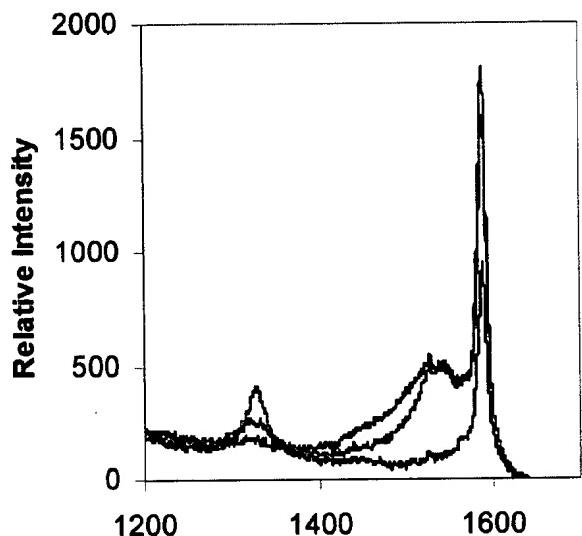


Fig. 1

A



B

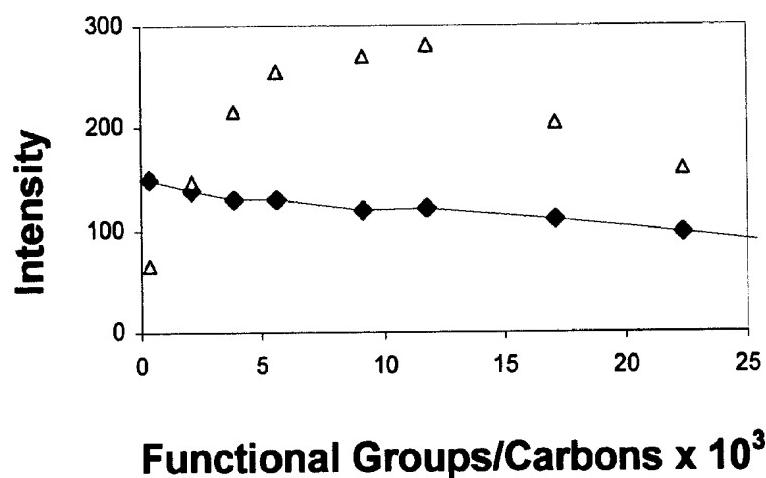


Fig. 2

Selectivity of Electronic Structure in the Functionalization of Single Walled Carbon Nanotubes

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Diazonium reagents are shown to functionalize single walled carbon nanotubes suspended in aqueous solution with high selectivity and enable manipulation according to electronic structure. For example, metallic species can be reacted to the near exclusion of semiconducting nanotubes under controlled conditions. Selectivity is dictated by the availability of electrons near the Fermi level to stabilize a charge transfer transition state preceding bond formation. The utility of this chemistry as a means of manipulating single walled carbon nanotubes by their electronic structure is demonstrated by the selective attachment of a phenol moiety and subsequent separation using electrophoretic means. The chemistry can be reversed using a thermal treatment that restores the pristine electronic structure of the nanotube.

The most significant hurdle to the widespread application of single walled carbon nanotubes is their manipulation according to electronic structure (1). All known preparative methods (2-4) lead to polydisperse materials of semiconducting, semi-metallic and metallic electronic types. Recent advances in the solution phase dispersion (5, 6) along with spectroscopic identification using band-gap fluorescence (7) and Raman spectroscopy (8) have greatly improved the ability to monitor electrically distinct nanotubes as suspended mixtures and have led to definitive assignments of the optical features of semiconducting (7), as well as metallic and semi-metallic species (8). In this work, we report the first selective reaction pathways of carbon nanotubes where covalent chemical functionalization (9) is controlled by differences in the nanotube electronic structure. We demonstrate the utility of these chemical pathways for manipulation of nanotubes of distinct electronic types by selective functionalization of metallic nanotubes. Controlling nanotube chemistry in this way allows for the separation of semiconducting from metallic and semi-metallic nanotubes with high selectivity and scalability: a long sought goal of the carbon nanotube community.

The diversity in electronic structure of carbon nanotubes arises from the unique quantinization of the electronic wavevector of the 1-D system through the conceptual rolling of a graphene plane into a cylinder forming the nanotube (2, 4). The vector in units of hexagonal elements connecting two points on this plane defines the nanotube chirality in terms of two integers: n and m . When $|n-m| = 3q$ where q is an integer, the nanotube is metallic or semi-metallic while remaining species are semi-conducting with a geometry dependent band-gap (10). Although largely unrealized in previous studies, subtle differences in geometric structure of carbon nanotubes lead to dramatic changes in the rates of solution phase reactivity of these species. We find that water soluble diazonium salts (11), which have been shown to react with carbon nanotubes (9, 12, 13), can extract electrons from nanotubes in the formation of a covalent aryl bond (Fig. 1A) and thereby demonstrate superb chemoselective reactions with metallic tubes over the semiconducting tubes. This bond forms with extremely high affinity for electrons with energies, ΔE_r , near the Fermi level, E_f of the nanotube (Fig. 1B). The reactant forms a

charge transfer complex at the nanotube surface, where electron donation from the latter stabilizes the transition state and accelerates the forward rate. Once the bond symmetry of the nanotube is disrupted by the formation of this defect, adjacent carbons increase in reactivity (Fig. 1C) and the initial selectivity is amplified as the entire nanotube is functionalized.

Under carefully controlled conditions (14), this behavior can be exploited to obtain highly selective functionalization of metallic and semi-metallic nanotubes to the exclusion of the semiconductors. Figure 2 shows the UV-vis-nIR absorption spectra of aqueous suspended nanotubes after successive additions of 4-chlorobenzenediazonium tetrafluoroborate after steady state. The spectrum monitors the $v_1 \rightarrow c_1$ electronic transitions of the metallic and semi-metallic nanotubes from roughly 440 to 645 nm as well as the $v_1 \rightarrow c_1$ and $v_2 \rightarrow c_2$ of the semiconducting nanotubes in the ranges from 830 to 1600 nm and 600 to 800 nm respectively. These separated absorption features allow for the monitoring of valence electrons in each distinct nanotube; as the species reacts to form covalent linkages, electrons are localized and these maxima decay. In Fig. 2, we note that under controlled additions only metallic transitions initially decay, indicating highly preferential functionalization of metallic nanotubes. This selectivity is remarkable given that these transitions arise from electrons that are much lower in energy compared to the $v_1 \rightarrow c_1$ and $v_2 \rightarrow c_2$ transitions of the semiconductors. The selective decay of these metallic transitions is unprecedented, and identifies this process as distinct from reversible electronic withdraw (15) or generic “doping” processes (16) as previously reported. Selectivity is also confirmed by the preservation of band-gap fluorescence of the semi-conducting nanotubes, which is known to be highly sensitive to chemical defects.

The functionalization increases the intensity of a phonon mode at 1330 cm^{-1} in the Raman spectrum as shown in Fig. 3A at 532 nm excitation. Its presence confirms the conversion of an sp^2 C to an sp^3 C on the nanotube during the formation of an sp^3 C- sp^2 C nanotube-aryl bond. This mode increases sharply with increasing functionalization, then decreases along with the C-C tangential mode as the system loses its electronic

resonance (Fig. 3B). These results allow, for the first time, a spectroscopic correlation of the number of sidewall functionalization events to this phonon intensity at low conversion, and will be valuable for the control of nanotube sidewall chemistry.

The addition of the moiety to the sidewall of the nanotube disrupts the radial phonon that gives rise to low frequency Raman lines distinct for species of a particular diameter which causes the mode to decay accordingly as the particular (n,m) nanotube reacts. Figure 4 analogously shows the solution phase Raman spectra at 532 nm of the mixture with each reactant addition after steady state and the relative rates of the decays of these features reveals unprecedented reactivity differences between chiral semi-metallic species. Here, Raman spectroscopy probes nanotubes with nearly identical transition energies and these differences reveal a curvature dependent stabilization of the charge transfer complex that may ultimately be exploited to separate semi-metallic and metallic species. We note that when all $v_1 \rightarrow c_1$ transitions of semi-metallic and metallic species have decayed (Fig. 2), and only one low frequency Raman mode that we have previously assigned to the (9,2) semiconductor (15) remains unaffected. This serves as the first independent confirmation of the recent spectroscopic assignment of these features (7, 8).

Carbon nanotube chemistry has been correctly described using a pyramidization angle formalism (17). Here, chemical reactivity and kinetic selectivity are related to the extent of s character due to the curvature-induced strain of the sp^2 -hybridized graphene sheet. Because strain energy per carbon is inversely related to nanotube diameter, this model predicts smaller diameter nanotubes to be the most reactive, with the enthalpy of reaction decreasing as the curvature becomes infinite. While this behavior is most commonly the case, this work in contrast underscores the role that the electronic structure of the nanotube has in determining its reactivity. Because such structure is highly sensitive to chiral wrapping, chemical doping, charged adsorbates as well as nanotube diameter, there exists a considerable diversity of these various pathways in addition to a simple diameter dependence.

Selective functionalization as a handle for nanotube separations is unique in that it allows manipulation independent of tube length unlike chromatographic based methods. Because the selectivity is nearly complete, this chemistry can form the basis for high efficiency separations in contrast to the minor enrichments that have been reported to date (18, 19). We have phenolated the sidewalls of metallic nanotubes with approximately 0.11 sidegroups per carbon and fractionated samples using electrophoretic means. Above a pH of 10.2, these groups are deprotonated leaving a net negative charge per group on the nanotube (Fig. 5A). A non-ionic surfactant was used in this case to enhance the electrostatic changes upon functionalization. We measured the change in electrophoretic mobility μ upon reaction using migration velocities during capillary electrophoresis (CE). This mobility is the observed velocity v normalized to the field strength across the capillary E and equal to:

$$\mu = \frac{v}{E} = \frac{q}{f}$$

where q is the net charge on the nanotube and f is a hydrodynamic resistance factor strongly dependent upon the length to diameter ratio (L/D) of the nanotube. The functionalization does not alter f since the length is unaffected, and the diameter of the tube is extended far less than the surfactant-adsorbed layer on the sidewall. However, the mobility is sensitive to charged groups at the nanotube surface.

Unfunctionalized nanotubes in Triton X-405 consistently show 3 distinct populations when fractionated by an applied electric field: those with δ^+ charge from the adsorption of the cationic buffer molecules, those that are neutral and δ^- from surface -OH and -COOH groups on the sides and ends of the tubes from processing. Partitioning between these three groups depends on the balance of cationic adsorption and anionic functionalities. Fig. 5A is a CE trace of unfunctionalized and phenol-functionalized material showing differences in migration times of 2 min. Deuterium oxide provides a neutral marker with species migrating later than this time being negatively charged.

Scaling of the migration velocity by the applied field allows for a comparison of electrophoretic mobility distributions (towards the positive electrode) between reacted and unreacted nanotubes. In Fig. 5B, this comparison demonstrates how functionalized material is extracted from the total population by exploiting this change in mobility due to the negative charge.

Thermal pyrolysis of the reacted material at 300°C in an atmosphere of flowing inert gas cleaves the aryl moieties from the sidewall and restores the spectroscopic signatures of the aromatic, pristine nanotubes (9). Fig. 6 compares the Raman spectra before and after recovery and thermal pyrolysis at 633 nm (Fig. 6). This wavelength was employed because it probes a mixture of metals and semi-conductors for samples prepared by CO disproportionation (8). The radial phonon modes are nearly completely restored after thermal treatment. Similarly, electronic transitions in the absorption spectrum are restored indicating the loss of the side group and a restoration of the original electronic structure of the nanotube. Hence this selective chemistry can be used as a reversible route to separate, deposit or chemically link nanotubes of a particular electronic structure and the original optical and electronic characteristics can then be recovered.

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Figure Captions

Figure 1: A) Diazonium reagents extract electrons, thereby evolving N₂ gas and leaving a stable C–C covalent bond with the nanotube surface. B) The extent of electron transfer is dependent upon the density of states in that electron density near the Fermi level leads to higher initial activity for metallic and semi-metallic nanotubes. C) The induced defect increases the reactivity of surrounding carbon atoms. Hence the initial single site selectivity is amplified allowing extensive functionalization of nanotubes according to their electronic structure.

Figure 2: A) UV-vis-nIR Spectrum of sodium dodecylsulfate suspended carbon nanotubes after the addition of various amounts of 4-chlorobenzenediazonium tetrafluoroborate (in mol/mol carbon.) Under controlled conditions, semiconductor transitions are unaffected while metals react with high selectivity. B) Expanded view of the metallic region. The tetrafluoroborate salt causes some bathochromic shifting of the longer wavelength features due to changes in the surfactant adsorbed phase.

Figure 3: A) Raman spectrum at 532 nm excitation showing the growth of the “disorder” mode with increasing functionalization from 0 (black), 5.6 (blue), to 22.4 (red) groups attached per 1000 carbon atoms. B) The intensity of the tangential mode (blue) x 0.1 decreases as resonance enhancement of the scattering event is lost with increasing reaction. The disorder mode (yellow) increases sharply then decays due to the same loss of enhancement.

Figure 4: A) Low wave-number Raman spectra at 532 nm excitation of the starting solution. Four metallic nanotubes (black) are probed at this wavelength and one semiconductor (red) via a radial mode sensitive to nanotube diameter. B) After 5.6 groups attached per 1000 carbons, functionalization disrupts this mode as seen by the decay of particularly the small diameter metals. This first evidence of selective reactivity among metals provides a handle for separation of these species. C) After a ratio of 22.4, all metallic modes have decayed leaving only the single semiconductor in agreement with Fig 2b.

Figure 5: A) Selective phenolation of nanotubes in water allows for a control of surface charge via pH cycling to 10.4; B) Capillary electrophoresis can then be used to separate charged and uncharged nanotubes. The neutral marker is measured by injecting D₂O. Traveling from + to – charge, functionalized material (dotted lines) migrate 2 min. slower than unfunctionalized neutral material (solid). C) The electrophoretic mobility distribution of both the reacted (dotted) and unreacted (solid) material shows the increase in negative charge due to the functional groups.

Figure 6: Raman spectra at 633 nm probing both metals and semi-conducting nanotubes before reaction (solid) and after recovery and thermal pyrolysis (dotted.) The reversibility of the chemistry means that intrinsic electronic and optical properties of the pristine nanotubes can be recovered.

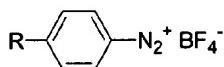
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14. A recirculating flow reactor was used to transfer 150 mL/min of sodium dodecyl sulfate suspended carbon nanotubes through a cuvettes with inlet and outlet ports. Continuous UV-vis-nIR spectra were generated after the addition of a metered amount of diazonium aryl chloride tetrafluoroborate. Addtions were made in 0.05 mM incriments after the system arrived at steady state.
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CLAIMS

What is claimed is:

1. A method for selectively functionalizing carbon nanotubes comprising:
 - a) suspending a plurality of carbon nanotubes in a solvent; and
 - b) reacting an effective amount of a diazonium species with the suspended carbon nanotubes such that a portion of the carbon nanotubes react preferentially with said diazonium species based on the electronic properties of the carbon nanotubes comprising said portion.
2. A method for selectively functionalizing carbon nanotubes comprising:
 - a) adding a plurality of carbon nanotubes to an aqueous surfactant solution and homogenizing to form a mixture of surfactant-suspended carbon nanotubes; and
 - b) reacting an effective amount of a diazonium species with the surfactant-suspended carbon nanotubes such that a portion of the carbon nanotubes react preferentially with said diazonium species based on the electronic properties of the carbon nanotubes comprising said portion.
3. The method of Claims 1 or 2, wherein the carbon nanotubes are selected from the group consisting of single-wall carbon nanotubes, multi-wall carbon nanotubes, and combinations thereof.
4. The method of Claim 2, wherein the surfactant is selected from the group consisting of ionic surfactants, non-ionic surfactants, cationic surfactants, anionic surfactants, sodium dodecyl sulfate (SDS), sodium dodecylbenzene sulfonate (SDBS), sodium octylbenzene sulfonate, Triton X-100, dodecytrimethylammonium bromide (DTAB), and combinations thereof.
5. The method of Claims 1-3 or 4, wherein the diazonium species is an aryl diazonium salt.
6. The method of Claim 5, wherein the aryl diazonium salt comprises:



and wherein R is selected from the group consisting of halogen, nitro, cyano, alkyl, aryl, arylalkyl, hydroxy, carboxylic ester, carboxylic acid, thiocarbonate, amide, alkoxy, polyether, polyalkyl, hydroxy alkyl, and combinations thereof.

7. The method of Claim 6, wherein R is hydroxy.
8. A method for separating carbon nanotubes on the basis of their electronic bandgap comprising:
 - a) functionalizing carbon nanotubes according to the method of Claim 7 to yield a mixture of selectively-functionalized surfactant-suspended carbon nanotubes, wherein a portion of the carbon nanotubes within the mixture have been selectively-functionalized;
 - b) deprotonating the hydroxy groups present in the mixture of selectively-functionalized surfactant-suspended carbon nanotubes by increasing pH; and
 - c) electrophoretically separating the functionalized carbon nanotubes from the unfunctionalized carbon nanotubes.
9. The method of Claim 8, wherein the electrophoretic means is selected from the group consisting of gel electrophoresis, capillary electrophoresis, and combinations thereof.
10. The method of Claims 8 or 9, further comprising a thermal defunctionalization step to regenerate separated, unfunctionalized carbon nanotubes.
11. A composition of functionalized carbon nanotubes of specific electronic type, made by the method of Claim 8.
12. A composition of carbon nanotubes of specific electronic type, made by the method of Claim 10.

ABSTRACT

The present invention is directed toward a method of selectively functionalizing carbon nanotubes of a specific type or range of types, based on their electronic properties, using diazonium chemistry. The present invention is also directed toward methods of separating carbon nanotubes into populations of specific types or range(s) of types via selective functionalization and electrophoresis, and the novel compositions generated by such separations.

Figure 1

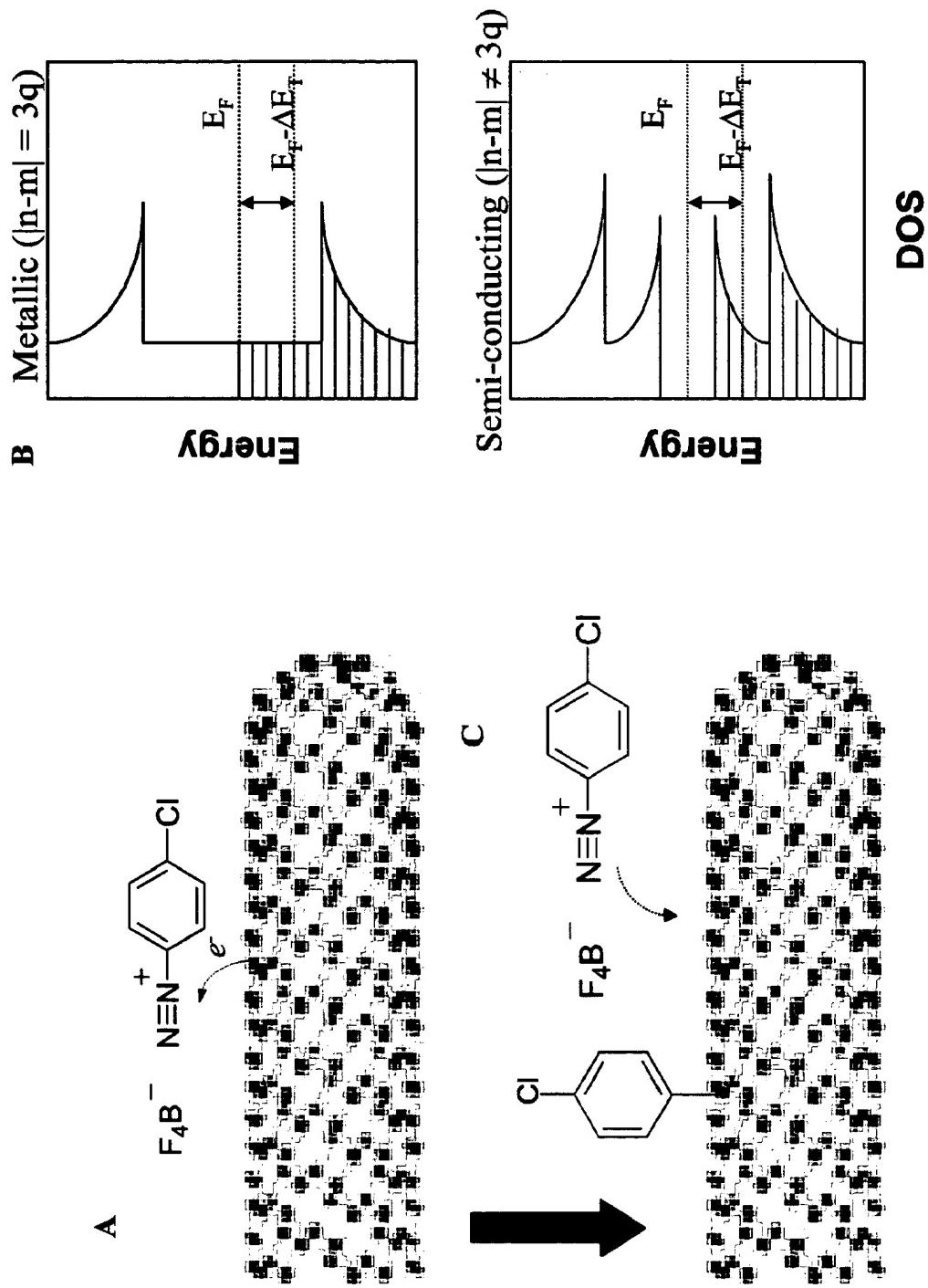


Figure 2

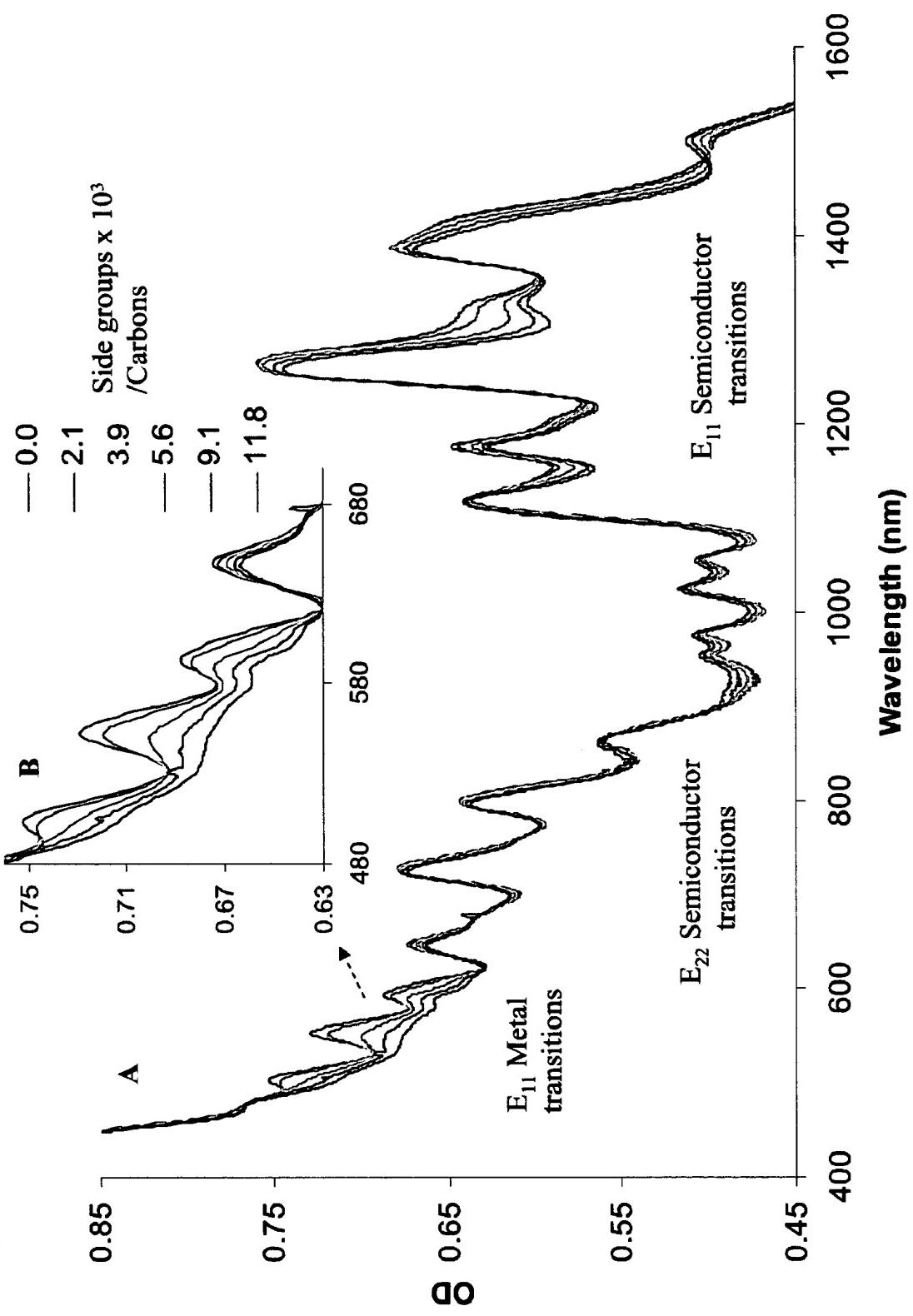


Figure 3

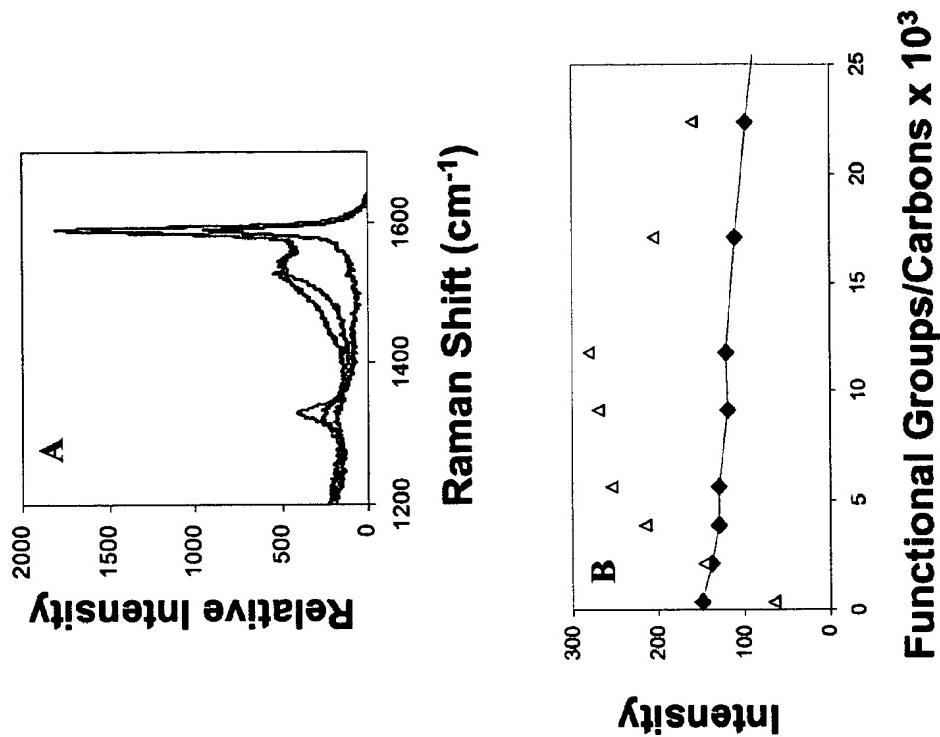


Figure 4

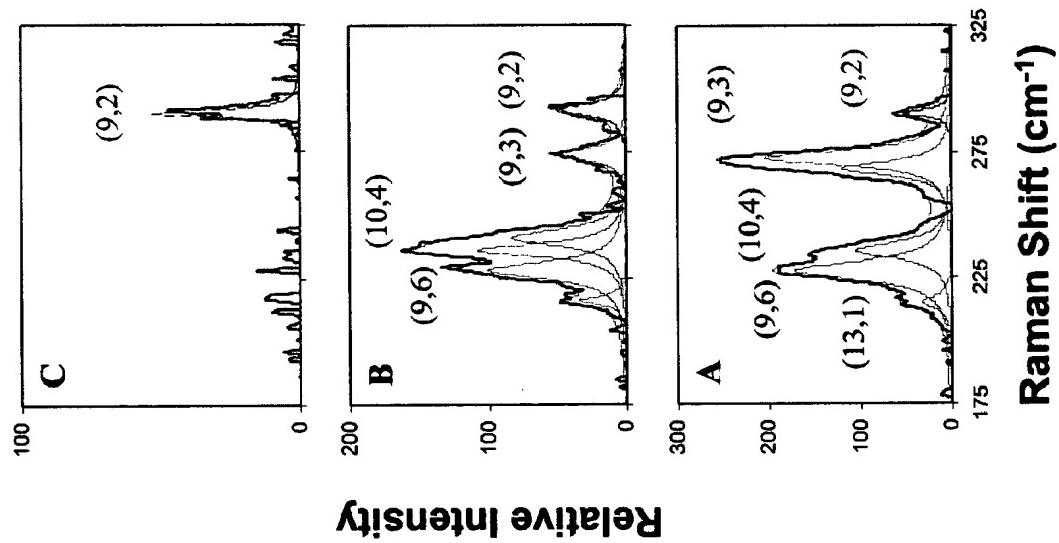


Figure 5

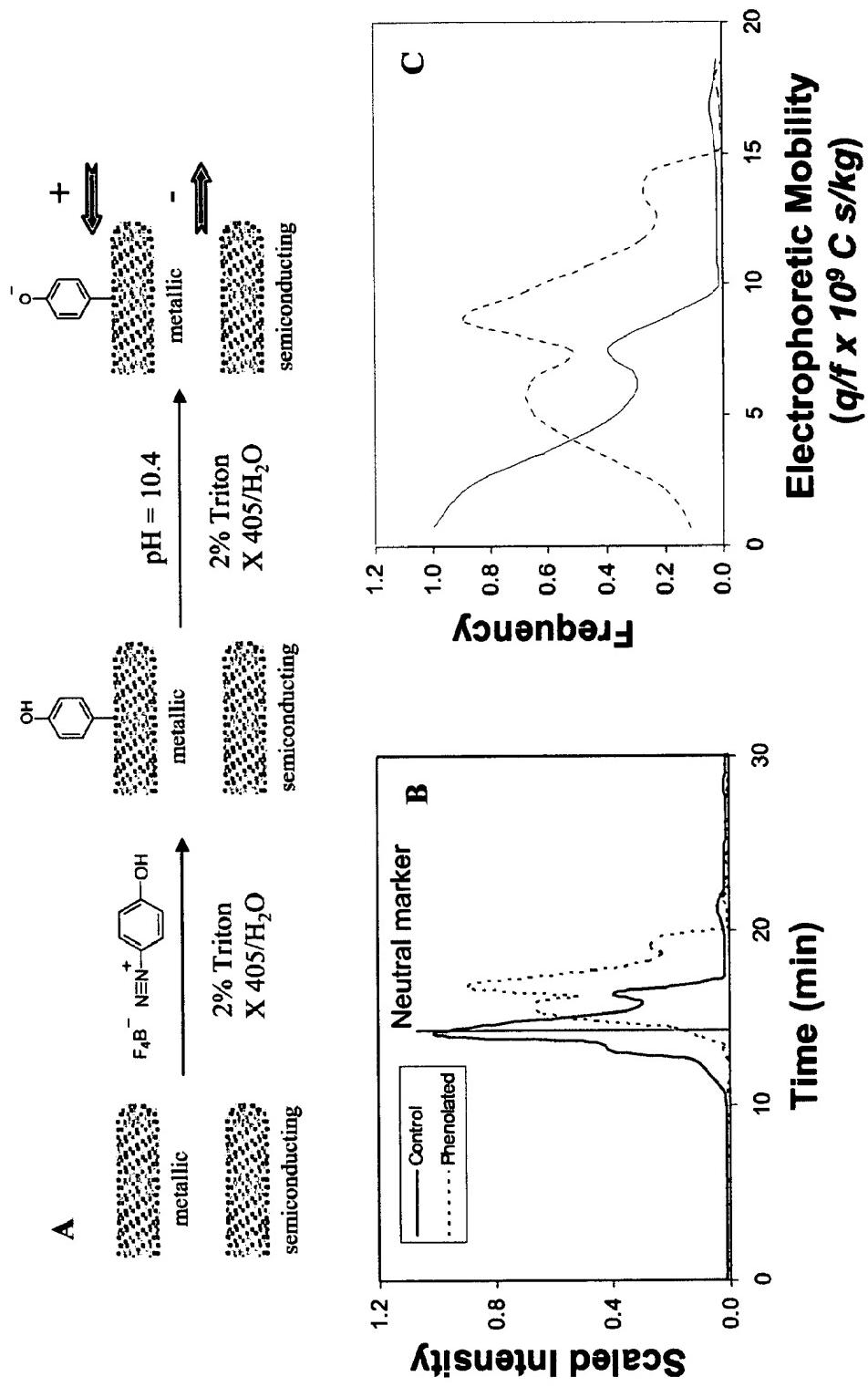
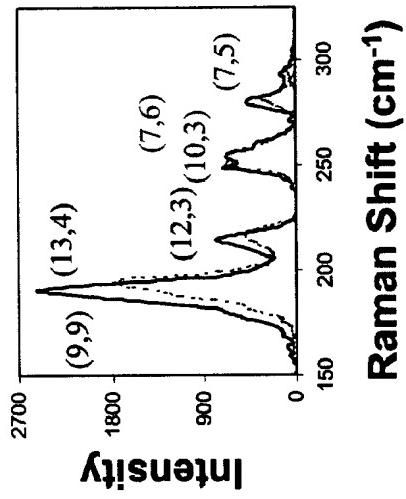


Figure 6



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